

CARBON BASED ELECTROCHEMICAL CAPACITORS: BEYOND CAPACITIVE STORAGE

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Introduction

Electrochemical capacitors EC are the devices based on the reversible storage of energy by electrostatic (capacitive) attraction of ions. Performance of EC are strongly governed by the type of carbon materials but also kind of electrolytes, namely aqueous (acidic, basic, neutral), organic and ionic liquids. As a consequence, practical voltage range of EC in these electrolytes varies from 0.8 V to 3.5 V, respectively. The type of current collector will also affect EC voltage values.

Capacitive charge storage can be increased by faradaic reactions, frequently called pseudocapacitive effects. It must be underlined that only redox reactions which present capacitive behavior should be considered, i.e., capacitance should be proportional to the charge accordingly to formula $C = dQ/dE$. Faradaic contribution can be originated from electrode materials but also from electrolytic solutions.

Exploring redox active species from electrolytic solution is an attractive possibility for energy increase [1-3]. Practical application of such redox pairs will be determined by reversibility, pH of solution, concentration, price, availability, toxic character. Some of them can be used only as additive to electrolyte. Taking into account their redox potential and size, different species could be used for positive and negative electrode. Porosity of carbon materials plays a crucial role, hence, it should be adapted to redox species. Obviously size pores of carbon should much ions size (cations and anions) taking into account solvation shell, however, ions could also be sorbed in partly and/or fully desolvated state.

Experimental

Activated carbon materials in the form of powder or tissue (ca. 10 mg per electrode) have been used for EC assembly. Aqueous electrolytes of neutral character such as iodide (1M KI), nitrate (1M NaNO₃) and sulphate (1M Li₂SO₄) have been selected to minimize a corrosive effect on current collector. Physico-chemical analyses of carbon materials (porosity and structure) and electrolyte (pH and conductivity) have been performed prior to the electrochemical measurements. The systems were aged with two methods: galvanostatic cycling and potentiostatic floating. Specific capacitance values have been controlled in time together with internal resistance. After reaching 20% capacitance fade, the systems were disassembled and post mortem analysis such as nitrogen adsorption/desorption was performed at 77K (Micromeritics ASAP 2460). Raman spectroscopy with 633 nm laser (DXR™ 2 Raman Microscope Thermo-scientific) was carried out to monitor structure changes. During some experiments the pressure of gases evolved has been measured in a specially designed electrochemical cell.

Results and Discussion

The optimal voltage of capacitor based on porous activated carbon operating in aqueous neutral electrolytes was 1.6 V. Typical galvanostatic charging/discharging with 1 A/g current load and floating tests (with 2 hours polarization at 1.5 V) were performed in various electrolytes. The end-of-life criterion (80% of initial capacitance retained) was the same for two procedures. Both ageing methods performed in 1M KI affect the electrode porosity [3]. Specific surface area of carbon electrodes dropped significantly from 1840 m²/g to 800 m²/g, especially for positive electrode aged by floating (**Fig. 1**). It was proved that floating is much more ageing-effective for the system as its operation time for reaching the same end-of-life criterion is almost 3 times shorter than in the case of cycling. Scanning Electron Microscopy images proved existence of a deposit on the both aged electrodes independently on the kind of test. This deposit was at the origin of pores blockage, increase of resistivity (ESR) from 0.42 to 1.77 Ohm, in turn, capacitor failure especially after floating test.

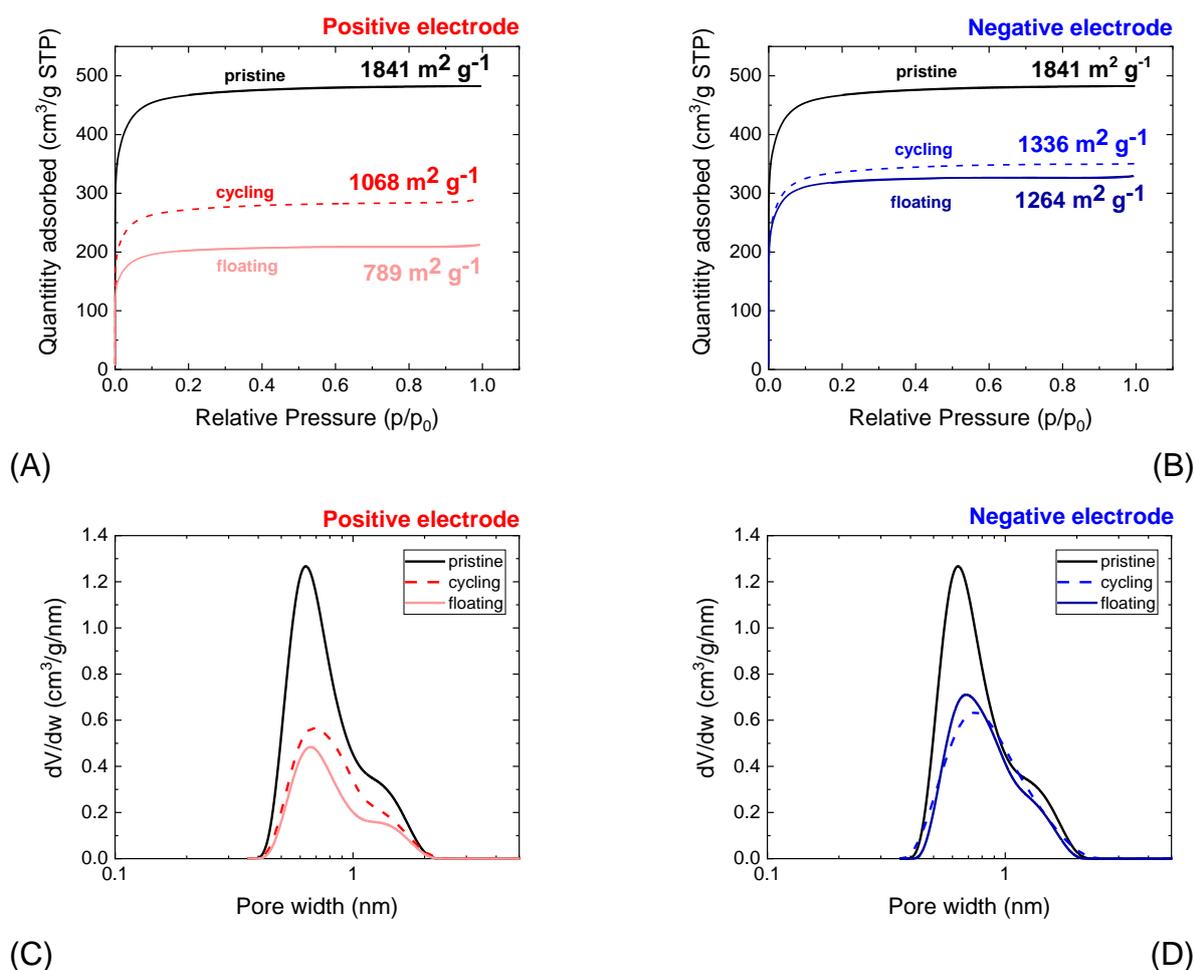


Figure 1. Post-mortem physico-chemical analysis of electrode materials: A) and B) N_2 adsorption/desorption isotherms for positive and negative electrodes with S_{BET} values; C) and D) pore size distribution (2D-NLDFT) for both electrodes. Electrolyte: 1M KI.

Conclusions

- Carbon pores are drastically blocked by inorganic deposit depending on the type of electrolyte and electrode polarity during long-term cycling.
- Floating is more detrimental technique for carbon electrodes *versus* galvanostatic cycling.

Acknowledgments

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References

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